Excited-state proton transfer of 4-hydroxyl-1, 8-naphthalimide derivatives: A combined experimental and theoretical investigation

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Abstract

The photophysical properties of N-butyl-4-hydroxyl-1, 8-naphthalimide (BOH) and N-(morpholinoethyl)-4-hydroxy-1, 8-naphthalimide (MOH) in various solvents are presented and the density functional theory (DFT) / time-dependent density functional theory (TDDFT) methods at the B3LYP/TZVP theoretical level are adopted to investigate the UV–visible absorption and emission data. An efficient intermolecular excited-state proton transfer (ESPT) reaction occurs for both compounds in DMSO, methanol and water. In aqueous solution, both BOH and MOH can be used as ratiometric pH probes and perform as strong photoacids with $\text{pK}_a^* = -2.2, -2.4$, respectively. Most interestingly, in the steady-state fluorescence spectra of BOH and MOH in concentrated HCl, an unexpected blue-shifted band is observed and assumed to originate from the contact ion pair (CIP) formed by hydronium ion and the anionic form of the photoacid resulted from ESPT. Theoretical calculations are used to simulate the CIP in the case of BOH, which afford reasonable results compared with the experimental data.

Keywords:

Naphthalimide

Excited-state proton transfer

Photoacid

Contact ion pair

Time-dependent density functional theory

1. Introduction

Upon photoexcitation, aromatic alcohols (ROH) such as naphthols, hydroxyquinolines, and hydroxypyrenes may increase the acidity dramatically. Research on this photoinduced deprotonation is first described by Förster in 1949 [1] and still attracting intensive attention in the field of biology and physical chemistry [2-11]. The Eigen-Weller model for proton transfer is used to depict this process, where the initial short-range proton transfer forms a contact ion pair (CIP) as a reaction intermediate followed by diffusion controlled separation of the ions [12-13].

Recently, Brouwer and coworkers synthesized and characterized some hydroxy-substituted 1, 8-naphthalimide derived “super” photoacids, where the hydroxyl group is located at the 3 or 6 position of the naphthalimide ring [6, 14]. However, for 4-hydroxyl-1, 8-naphthalimide derivatives, which are extensively used for designing turn-on or ratiometric fluorescent indicators for bioimaging [15-29], the photophysical properties and the excited-state proton transfer (ESPT) reactions are rarely studied [30].

In this contribution, the steady-state absorption and emission spectra of two 4-hydroxyl-1, 8-naphthalimide derivatives (BOH and MOH, Scheme 1) in organic solvents and water with various pH values are recorded. The density functional theory (DFT) / time-dependent density functional theory (TDDFT) methods at B3LYP/TZVP theoretical level are adopted to investigate the UV-visible absorption and emission data. In the study of the ESPT of 5-cyano-2-naphthol in sub- and supercritical water, Kobayashi and coworkers [31] found that the band of their excited neutral (ROH^*) and anionic (RO^{*-}) species were replaced by a single band of unknown X^* in the steady-state fluorescence spectra; they assigned the fluorescence of their unknown chemical species as CIP; however, their attempts of using theoretical calculations to gain a stable structure as the direct evidence for the existence of the CIP failed. In this paper, we present the observation of an unexpected blue shifted single band in the fluorescence spectra of BOH and MOH in concentrated HCl, which is distinct from the fluorescence of the neutral or anionic species and is assumed to emit from the CIP resulted from the ESPT reaction. Meanwhile, the DFT/TDDFT methods were used to gain more insight into the CIP formed by BO^{*-} and hydrated proton. The calculated absorption and fluorescence peaks were used to test the proposed CIP models by comparing with our experimental data. The structural changes of the hydrogen-bonded complexes from the ground-state (S_0) to the first excited-state (S_1) and the potential curves of the ESPT reaction along the hydrogen-bond coordinate are also discussed.

Scheme 1 Chemical structures of BOH and MOH

2. Experimental section

2.1. Instruments and Materials

Steady-state UV-visible absorption spectra were measured on a Lambda 35 UV-visible Spectrophotometer (Perkin-Elmer) with matched 10-mm quartz cuvettes. Fluorescence spectra were obtained from Fluoromax-4 Spectrofluorometer (Horiba-Jobin Yvon, monochromator calibrated). Except for the samples in H_2SO_4 aqueous solutions ($17 \pm 1^\circ\text{C}$), all the other experiments were performed at room temperature ($26 \pm 1^\circ\text{C}$).

Acetonitrile, toluene, dimethylsulfoxide (DMSO), dichloromethane (DCM) and methanol were purchased from reputable suppliers and used as received (HPLC grade). Ultrapure water (resistivity

18.2 M Ω ·cm) from a Millipore water purification system was used throughout. All the solvents were checked for fluorescent impurities prior to use. Other chemicals were of analytical grade without further purification. Phosphate buffer (50 mM) with various pH values were prepared by mixing the aqueous solutions of monosodium phosphate (50 mM), sodium hydrogen phosphate (50 mM) or phosphoric acid (50 mM), measured with an Ohaus pH meter STARTER2100. Phosphate buffer saline (PBS) was aqueous solution of phosphate (10 mM), NaCl (8.0 g/L) and KCl (0.2 g/L), pH 7.3. Spectra in phosphate or HCl aqueous solutions were collected from samples of BOH and MOH diluted from their DMSO stock solutions.

The 4-hydroxyl-1, 8-naphthalimide derivatives (BOH and MOH) were synthesized following procedures described in the literatures [17, 22]. NMR and mass spectra were recorded to characterize the compounds. For BOH: ^1H NMR (500 MHz, d^6 -DMSO) δ (ppm): 11.84 (s, 1 H), 8.50 (dd, J = 8.5 Hz, 1 H), 8.43 (dd, J = 7.0 Hz, 1 H), 8.33 (d, J = 8.0 Hz, 1 H), 7.73 (t, J = 7.8 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1 H), 4.01 (t, J = 7.5 Hz, 2 H), 1.63-1.57 (m, 2 H), 1.39-1.32 (m, 2 H), 0.94 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (126 MHz, d^6 -DMSO) δ (ppm): 13.63, 19.76, 29.69, 39.02, 109.85, 112.56, 121.71, 122.29, 125.41, 128.73, 129.07, 130.95, 133.37, 160.13, 162.89, 163.56. MS (API-ES): m/z , Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: 269.11, found: $[\text{M}-\text{H}]^-$ 268.16. For MOH: ^1H NMR (400 MHz, d^6 -DMSO) δ (ppm): 8.53 (dd, 1H, J = 8.2 Hz), 8.46(dd, 1H, J =7.2 Hz),8.35 (d, J =8.4 Hz, 1H), 7.77-7.73(m, 1H), 7.13(d,1H, J =8.0 Hz), 4.17 (t, 2H, J =7.0 Hz), 3.55 (t,4H, J =4.6 Hz), 2.60-2.50 (m,6H). ^{13}C NMR (d^6 -DMSO, 100 MHz) δ (ppm): 164.20, 163.47, 161.26, 134.13, 131.61, 129.77, 129.48, 125.96, 123.02, 122.21, 112.65, 110.57, 66.58, 56.12, 53.82, 36.91. HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4$ $[\text{MH}^+]$ 327.1345, found 327.1358.

2.2. Theoretical calculation details

DFT and TDDFT methods were used to do theoretical simulations in this work with Gaussian09 programs [32]. The Becke's three-parameter hybrid exchange functional with a Lee–Yang–Parr gradient-corrected correlation (B3LYP) [33] was used as a method of choice. The triple- ζ valence quality with one set of polarization functions (TZVP) basis sets [34] were used in all the calculations. Environmental effects (here, water or acetonitrile, as in the experiment) were accounted for using the IEFPCM solvation model. The vertical excitation and emission energies are based on the optimized geometries with no constraints to all the atoms, bonds, angles or dihedral angles during the optimizations. Vibrational frequencies are analyzed to confirm the validity of the stationary points.

3. Results and discussion

3.1. Spectra in organic solvents

Emission spectra of BOH and MOH in several organic solvents are presented in Fig. 1. There is only one fluorescence band emitted by ROH* in DCM, toluene or acetonitrile, while in DMSO or methanol, two fluorescence bands which are assigned to ROH* and RO⁻* are monitored. In DMSO or methanol, the absorption spectra indicate that both RO⁻ and ROH exist in the ground-state (Fig. S1, S2). In the presence of HCl (12 mM) in DMSO or methanol, the compounds predominately exist as the neutral forms in the ground state; however, there are still two emission bands in the spectra of those solutions (Fig. S3). Thus, it is evident that BOH and MOH undergo ESPT reactions efficiently in DMSO or methanol, but not in DCM, toluene or acetonitrile.

Fig. 1. Normalized fluorescence spectra of (a) BOH and (b) MOH in organic solvents (the excitation wavelength, $\lambda_{ex} = 355$ nm). The concentrations of these solutions are $10^{-6} \sim 10^{-5}$ M.

The absorption and fluorescence spectral properties of the two compounds in the above solvents, including the absorption and fluorescence maxima (λ_a , λ_f), the fluorescence quantum yield (Φ_f) values, are summarized in Table 1. The absorption maxima for samples in DMSO and methanol, where both the neutral and anionic forms exist, are determined by spectral decomposition with a sum of two gaussians. As for the emission data, we noted that Brouwer and coworkers reported the requirement of three rather than two gaussians to fit the fluorescence spectrum of **EG-dHONI** in DMSO [6]; in our case, a sum of three gaussians was required to fit the curves for samples in DMSO and methanol (Fig. S4), since two gaussians were not adequate to model the spectra (Fig. S5).

Table 1

Photophysical properties of BOH and MOH in organic solvents

Solvent	BOH			MOH		
	λ_a /nm	λ_f /nm	Φ_f^a	λ_a /nm	λ_f /nm	Φ_f^a
Toluene	360	420	0.97	361	415	0.040
DCM	360	425	1.0	363	436	0.033
Acetonitrile	365	440	0.78	365	442	0.053
DMSO	376 ^b , 483 ^c	467, 550	0.02	376 ^b , 483 ^c	470, 552	0.15
Methanol	378 ^b , 453 ^c	460, 543	0.082	378 ^b , 453 ^c	467, 545	0.056

^a Φ_f values are determined by referring to sulfate quinine in 0.05 M H₂SO₄ ($\Phi_f = 0.55$) [35]. The confidence is $\pm 10\%$.

^{b,c}Data of the neutral and anionic forms determined by decomposition of the absorption spectra with a sum of two gaussians.

In contrast to BOH, the Φ_f values of MOH in aprotic solvents such as toluene, DCM or acetonitrile are substantially small. To investigate this effect of substitution, theoretical calculations were carried out by using the Gaussian 09 program with acetonitrile as a representative solvent (Table 2). It is revealed that the fluorescence of MOH is quenched by photoinduced electron transfer (PET) from the morpholine group to the naphthalimide ring, whereas no PET happens in the case of BOH. The calculated absorption peaks for MOH and BOH are in good agreement with the experimental data. Obviously, the highest occupied molecular orbital (HOMO) of MOH is located at the morpholine group while the lowest unoccupied molecular orbital (LUMO) is located at the naphthalimide ring; the small oscillator strength ($f = 0.0011$) of $S_0 \rightarrow S_1$ implies a forbidden electronic transition, indicating that the S_1 state of MOH is a dark state rather than an emissive state. Absence of the morpholine group for BOH makes the transition $S_0 \rightarrow S_1$ allowed ($f = 0.2659$). The satisfactory agreement between the experimental and calculation results indicates that the DFT/TDDFT methods used here is suitable for the investigation.

Table 2

Calculated properties of electronically excited states by TDDFT/B3LYP/TZVP, based on the optimized S_0 state geometries of MOH and BOH with acetonitrile as a solvent.

Compd	Electronic transition	λ_a	Oscillator strength (f)	Composition	Contribution
MOH	$S_0 \rightarrow S_1$	394 nm	0.0011	HOMO	LUMO 99.6%

BOH	$S_0 \rightarrow S_2$	365 nm	0.2757	HOMO-1	LUMO 97.1%

BOH	$S_0 \rightarrow S_1$	365 nm	0.2674	HOMO	LUMO 97.3%

3.2. Spectra in phosphate buffer

Next, we investigated the ESPT reactions in water. As shown in Fig. 2a, with pH decrease, the absorption spectra of BOH change continuously with an isosbestic point at ca. 405 nm, reflecting the steady-state protolytic equilibria. The pKa value of BOH is determined to be 5.8 by referring to the Henderson–Hasselbach-type mass action equation. MOH undergoes similar absorption changes and exhibits a pKa of 5.3 (Fig. 2b).

Fig. 2. Absorption spectra of (a) BOH (13 μM) and (b) MOH (5 μM) at various pH values in aqueous solution. The inset graphs show the absorption at 447 nm (A_{447}) as a function of pH values. The experiment was conducted in phosphate buffer (50 mM) with 1% DMSO as a co-solvent.

The fluorescence emission and excitation spectra of BOH were obtained. As shown in Fig. 3a, unlike the appearance of two emission bands in DMSO or methanol, BOH shows only one fluorescence band peaked at ca. 548 nm in aqueous solutions (pH 2.58 ~ 10.55). Calculated by TDDFT/B3LYP/TZVP, the fluorescence peaks of BOH* and BO⁻* in water are predicted to be 428 nm ($f = 0.2208$) and 540 nm ($f = 0.2208$), respectively. Thus the 548 nm fluorescence must come from BO⁻*. Since the neutral form of BOH dominates at pH below 4.0 in the ground-state (Fig. 2a), it is crystal clear that at pH 2.58 the 548 nm fluorescence is emitted by BO⁻* resulted from an ESPT process. Due to this ESPT process and the steady-state protolytic equilibria, we can see in the excitation spectra (Fig. 2b) that, as the pH value increases in the range of 1.85-10.55, the fluorescence intensity at 550 nm decreases progressively with $\lambda_{\text{ex}} = 375$ nm and increases steadily with $\lambda_{\text{ex}} = 445$ nm. In the pH range of 5.65-7.43, there is a linear relationship between pH values and the 445/375-nm excitation ratios ($F_{445}^{550} / F_{375}^{550}$) with a linear coefficient (R^2) 0.9921. Fig. 3a shows that the emission spectra of BOH is pH sensitive; however, under the excitation light around 405 nm, the fluorescence intensity at 550 nm is rather stable even though pH changes. What's more, the 405 nm semiconductor laser is usually available for a confocal laser scanning microscopy (CLSM). Thus, for fluorescent probes based on the 4-hydroxyl-1,

8-naphthalimide derivatives, it may be helpful to diminish the effect of pH with the choice of the 405 nm laser as the light source during imaging with CLSM.

Fig. 3. (a) Fluorescence emission spectra of BOH (13 μ M) at various pH values, λ_{ex} = 380 nm. Note that the 438 nm peak is due to the Raman scattering. (b) The excitation spectra of BOH (13 μ M) at various pH values, λ_{em} = 550 nm. The inset shows the pH titration curve of $F_{445}^{550}/F_{375}^{550}$. The experiment was conducted in phosphate buffer (50 mM) with 1% DMSO as a co-solvent.

Interestingly, the fluorescence peak of MOH in phosphate buffer shifted smoothly from 548 nm at pH 9.37 to 553 nm at pH 1.89 under the 380 nm excitation light (Fig. 4a). This shift is not observed in the case of BOH, thus it should be attribute to the morpholine group of MOH. The anionic and zwitterionic forms of MOH are calculated to emit at 540 nm ($f = 0.2211$) and 542 nm ($f = 0.2192$) respectively. Therefore, it is proposed that the slight red-shift of the fluorescence band is contributed by the protonation of the nitrogen atom of the morpholine group. Due to this shift, in the pH range of 4.5-7.0, there is a linear relationship between pH and the 560/500-nm emission ratio, $F_{380}^{560}/F_{380}^{500}$ (Fig. 4a, inset). Meantime, there is also a linear relationship for MOH between the excitation ratios and pH values in the range of 5.29~7.47 (Fig. 4b).

Fig. 4. (a) Fluorescence spectra of MOH (5 μ M) at various pH values, $\lambda_{ex} = 380$ nm. The inset shows the pH titration curve of $F_{380}^{560} / F_{380}^{550}$. (b) The pH titration curve of $F_{445}^{550} / F_{380}^{550}$ in the aqueous solution of MOH (5 μ M), phosphate buffer (50mM) with 1% DMSO as a co-solvent.

By referring to N-butyl-4-butylamino-1, 8-naphthalimide in absolute alcohol ($\Phi_f = 0.81$) [36], the Φ_f values of BOH and MOH in phosphate buffer saline (PBS, pH 7.3) were determined to be 0.053 and 0.075, respectively. The Φ_f values are higher than those of the 1, 8-naphthalimide derived “super” photoacids reported in ref. 6 in water (< 0.005 in all cases) and comparable to some published pH fluorescent probes [37]. Thus, BOH and MOH could be used as dual-excitation ratiometric fluorescent probes allowing the measurement of the fluorescence intensity at two excitation wavelengths.

3.3. Spectra in aqueous solutions of HCl

To get results at lower pH, the fluorescence spectra of the 4-hydroxyl-1, 8-naphthalimide s were then investigated in aqueous solutions of HCl. As shown in Fig. 5, the emission from BO^* and MO^* is depressed and broadened by H^+ , probably via the adiabatic recombination between proton and RO^* [11]; meantime, the neutral emission keeps very weak and grows with the increase of HCl. By spectral decomposition, the neutral peaks are obtained as 458 nm and 464 nm, respectively (Fig. S6). The emission maxima of the anionic forms in water are determined as 548 nm and 553 nm from the smoothed spectra of BOH and MOH in water (pH 13.0) with direct excitation of the anion form

($\lambda_{ex} = 445$ nm). Using the published method described in ref. 38, the pK_a^* values for BOH and MOH in water are estimated to be -2.3 and -2.4 from the above parameters of [$pK_a = 5.8$, $\lambda_a = (378$ nm, 447 nm), $\lambda_r = (458$ nm, 548 nm)] and [$pK_a = 5.3$, $\lambda_a = (380$ nm, 446 nm), $\lambda_r = (464$ nm, 553 nm)], respectively.

Fig. 5. Fluorescence spectra of (a) BOH ($13 \mu\text{M}$) and (b) MOH ($5 \mu\text{M}$) at various pH values in HCl aqueous solutions with 1% DMSO as a co-solvent, $\lambda_{ex} = 380$ nm.

It is notable that a new fluorescence band peaked at 532 nm arises for BOH at $[\text{HCl}] = 7.9$ M and grows stronger in concentrated HCl (~ 12 M) with $\Phi_f = 0.097$ (Fig. 6a). A similar spectral evolution is observed for MOH, with $\lambda_{em} = 544$ nm and $\Phi_f = 0.052$ in concentrated HCl (Fig. 6b). The fluorescence intensity at 550 nm with excitation at 380 nm is plotted against $[\text{HCl}]$ to clearly show the decrease of the band from $\text{RO}^{\cdot-}$ and the increase of the new one in the case of MOH (Fig. 6b, inset). The formation of the new fluorescence band is also observed for samples in H_2SO_4 aqueous solutions (Fig. S7). Compared with Fig. 6, the peaks of the new bands in H_2SO_4 aqueous solutions show a slight blue-shift, which is due to the difference of the solvent property. BOH and MOH should survive from acidic conditions at room temperature, because both compounds are synthesized in refluxed concentrated HI (54%) [17, 22] and the absorption spectra of MOH in HCl from 0.01 M to 12 M keep almost

unchanged (Fig. S2b). Thus the new fluorescence bands in HCl should be attributed to some complexes.

Fig. 6. The growth of new peaks in the fluorescence spectra of (a) BOH (13 μ M) and (b) MOH (5 μ M) in HCl aqueous solutions (1% DMSO as a co-solvent), λ_{ex} = 380 nm. The inset shows the intensity at 550 nm for MOH with various concentrations of HCl.

According to the Eigen-Weller model for proton transfer, CIP is a reaction intermediate [$RO^{-*} \cdots H^+$] consumed via diffusion controlled separation into a solvated proton (hydronium ion) and a solvated anionic form of the excited photoacid [6, 12, 13]. It may be difficult for CIP to get separated in such an environment as concentrated HCl with lesser availability of free water molecule. From another point of view, following the Eigen-Weller model and the equilibrium movement principle, the concentration of CIP should be considerable when the concentration of H^+ is substantial to recombine with RO^{-*} . Thus we tend to believe that CIPs are the complexes that give the blue-shifted emission.

It should be noted that, in the study of the ESPT reactions of 5-cyano-2-naphthol in sub- and supercritical water, Kobayashi and coworkers found that the emission of their ROH^* or RO^{-*} was replaced by a band from an unknown X^* [31]. They assigned the fluorescence of the unknown chemical species as CIP. In our case, the emission spectra shows the growth of a new peak rather than a

shifting of the original peaks of ROH* and RO⁻*, therefore it is plausible to assume that the emission band of MOH or BOH in concentrated HCl originates from the CIP resulted from the ESPT process.

CIP and the free base are usually undistinguishable in the steady-state fluorescence spectra [39]. To the best of our knowledge, a resolved single-peak-shaped curve has never been reported for CIP in the steady-state fluorescence spectrum under room temperature. As mentioned above in water at elevated temperature and pressure, the authors discovered a CIP band in the steady-state fluorescence spectrum; however, attempts of using theoretical calculations based on their model to simulate the CIP failed to gain direct evidence for the existence of CIP in the excited-state. As discussed below, we show theoretical calculations to investigate the CIP in the BOH system.

It is reported that the transformation of the ESPT from a photoacid to water is effectively controlled by the size of the water cluster and “4” is a key number regarding the number of water molecules accepting the proton [40, 41]. As shown in Fig. 7, to model the CIP, 4 water molecules are connected to the proton donor group of BOH so that the structure of the hydrated proton is similar to that of the Eigen cation (H₉O₄⁺), where a H₃O⁺ core is symmetrically surrounded by 3 water molecules in room-temperature aqueous acidic solutions [42]; the butyl group is simplified as methyl to reduce computational costs. Also, since hydrogen bonding may play an important role in regulating the fluorescence property of a dye [43-47], the hydrogen bonding interactions between water molecules and the carbonyl groups of BOH (B₁ and B₂) are considered and ignored in model A and B, respectively, to investigate the effect on the calculation results. Based on the optimized structures, the model A is calculated to absorb at $\lambda_a = 384$ nm ($f = 0.2683$) and emit at $\lambda_f = 518$ nm ($f = 0.2662$); the agreement between the theoretical and experimental results ($\lambda_a = 383$ nm, $\lambda_f = 532$ nm) is reasonable. For model B, the calculated photophysical properties ($\lambda_a = 377$ nm, $f = 0.2541$; $\lambda_f = 515$ nm, $f = 0.2503$) are nearly as impressive as above.

Fig. 7. Proposed structures of the CIP models for BOH.

The TDDFT method has proven useful to theoretically investigate the hydrogen bonding interactions that occur in the excited-state [40, 43]. As shown in Table 3, for model A, from the optimized structure of the S_0 state to that of the S_1 state, the bond length of O_a-H_b increases from 1.01 Å to 1.59 Å, and concomitantly the bond length of O_c-H_b is shortened by 0.60 Å; these structural changes show the proton ejection and acceptance processes; B_1 and B_2 are weak both in the S_0 and S_1 states and therefore proton transfer reactions is not likely to happen in these sites. For model B without the presence of water molecules near the carbonyl groups, the ESPT process is also indicated with the length of O_a-H_b increased by 0.58 Å and O_c-H_b shortened by 0.62 Å.

Table 3

Bond lengths of the optimized structures of the CIP models depicted in Fig. 7.

		O _a -H _b	O _c -H _b	O _c -H _d	O _e -H _d	O _e -H _f	O _g -H _f	O _e -H _h	O _i -H _h	B ₁	B ₂
A	S ₀	1.01	1.61	1.00	1.67	0.98	1.82	0.98	1.82	1.87	1.86
	S ₁	1.59	1.01	1.40	1.07	1.01	1.59	1.01	1.59	1.84	1.80
B	S ₀	1.00	1.63	1.00	1.67	0.98	1.82	0.98	1.82	-	-
	S ₁	1.58	1.01	1.40	1.07	1.01	1.59	1.01	1.59	-	-

Furthermore, the ESPT reaction is followed by TDDFT to provide a quantitative description of the potential energy curve, which is explored using relaxed potential energy scan that constrains the proton transfer coordinate (the O_a-H_b bond length) and minimizes all the other coordinates at every scan point (Fig. 8). The activation barrier for the ESPT reaction is only 3.2 kcal/mol and 3.8 kcal/mol for model A and B respectively, which predicts that at room temperature the reaction should occur easily after photon absorption. It is reported that hydrogen-bonding can facilitate excited-state intramolecular proton transfer (ESIPT) [48]; our results indicate that the hydrogen bonding interaction may make the intermolecular ESPT reaction easier to happen. Moreover, by scanning the potential curve, we also notice that there are two stable structures for each model in the S₁ state. For model A, beside the structure discussed above, the other stable structure in the S₁ state that corresponding to the O_a-H_b bond length of 1.03 Å is also obtained and gives an calculated emission peak of 450 nm (f = 0.3172), which corresponds to the neutral form of BOH in water.

Fig. 8. Optimized energy profiles for S₁ and S₀ of model A and B along the phenolic O_a-H_b bond as obtained at the B3LYP/TZVP calculation level.

4. Conclusion

In this work, we have presented the steady-state absorption and emission spectra of two 4-hydroxyl-1, 8-naphthalimide derivatives (BOH and MOH) in various organic solvents and aqueous solutions. It is shown that both compounds undergo ESPT reactions in methanol, DMSO and water. The different emission data between the two compounds are explained theoretically by the DFT/TDDFT methods. In aqueous solution, both compounds can be used as ratiometric pH probes, and meantime they show strong photoacidity with negative pK_a^{*} values.

Nevertheless, an unexpected single-peak-shaped band is observed in the steady-state fluorescence spectra of MOH or BOH in concentrated HCl at room temperature, which has not been reported in the study of photoacids before; we also envision theoretically that this band originates from the CIP formed by the anionic form of the photoacid and the hydrated proton. These results have given valuable information about the structure and stability of the CIP in the Eigen–Weller model.

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Electronic supplementary information (ESI)

Electronic supplementary information (ESI) available: Additional absorption spectra of BOH and MOH, Cartesian coordinates for the optimized geometries. See DOI:

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